Possible Sign-Reversing s-Wave Superconductivity in Co-Doped $BaFe_2As_2$ Proved by Thermal Transport Measurements

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Thermal transport measurements have been performed on single-crystalline Co-doped $BaFe_2As_2$ down to 0.1 K and under magnetic fields up to 7 T. Significant peak anomalies are observed in both thermal conductivity and thermal Hall conductivity below T_c as an indication of the enhancement of the quasiparticle mean-free path. Moreover, we find a sizable residual T-linear term in thermal conductivity, possibly due to a finite quasiparticle density of states in the superconducting gap induced by impurity pair breaking. Our findings support a pairing symmetry compatible with the theoretically predicted sign-reversing s-wave state.

KEYWORDS: iron pnictide superconductor, Co-doped $BaFe_2As_2$, thermal transport, sign-reversing s-wave state

The symmetry of the order parameter is essential for identifying the superconducting pairing mechanism. In conventional superconductors (e.g., Al and Pb), the effective electron interaction is mediated by phonons, which gives rise to the isotropic s-wave pairing symmetry. On the other hand, electron pairs glued by magnetic interactions form unconventional pairing states: p-, d-wave states and so on. So far, such unconventional superconducting states have been found in a number of materials on the boarder between magnetism and superconductivity.[1] These findings suggest that a system close to magnetic instability provides a fertile field for unconventional superconductivity. A new family of superconductors containing layers of iron pnictides bear resemblance to unconventional superconductors such as high-T_c cuprates with a two-dimensional electronic structure and a magnetic order proximity to the superconducting phase.[2,3] Therefore, an exotic superconducting pairing state can be naively expected in this system. In fact, an intriguing pairing state of sign-reversing s-wave symmetry has been theoretically proposed.[4,5]

Here, we report the first thermal transport evidence of a novel pairing state in Co-doped $BaFe_2As_2$. In particular, we find a sizable residual T-linear term of the thermal conductivity, possibly due to the impurity-induced in-gap state. In addition, significant peak anomalies are observed in both thermal conductivity and thermal Hall conductivity originating from

the prominent enhancement of the quasiparticle (QP) mean-free path below T_c. The field dependence of the delocalized QP density of states is apparently different from that of nodal gap excitation. These observations all point to the fully gapped sign-reversing s-wave state.

Single-crystalline samples with the composition $Ba(Fe_{0.93}Co_{0.07})_2As_2$ were grown by the FeAs/CoAs self-flux method.[6] The substituted Co atoms donate extra electrons to FeAs layers as itinerant carriers without creating localized moments.[7] For thermal transport measurements, two different crystals with dimensions of $1 \times 0.4 \times 0.04$ mm^3 were used. A one-heater-two-thermometer steady-state method was used to measure thermal conductivity down to 0.1 K and up to 7 T. Heat current was always aligned within the ab plane of the sample, and the magnetic field is applied along the c-axis. The samples were cooled in a magnetic field to ensure field homogeneity. We used Cernox and RuO_2 thermometers above and below 1 K, respectively. The thermometers were thermalized on the sample by gold wires held by spot welding, providing a good thermal contact with a low electrical contact resistance, $R_c \leq 50$ mΩ, at 300 K. In fact, we confirmed ohmic thermal response with the applied power down to the lowest temperature. The same contacts and gold wires were used to measure the resistivity of the sample by a standard four-contact method.

First, we present the temperature dependence of the thermal conductivity $\kappa_{xx}(T)/T$ under several magnetic fields in Fig. 1. The arrow indicates T_c at zero field determined from the resistivity measurement shown in the upper inset of Fig. 4. Interestingly, $\kappa_{xx}(T)/T$ increases below T_c and reaches a maximum at 12 K ($\sim T_c/2$). In addition, the peak is suppressed by applying a magnetic field. In general, thermal conductivity is composed of the electronic term κ^{e}_{xx} and the phononic term κ^{ph}_{xx}; $\kappa_{xx} = \kappa^{e}_{xx} + \kappa^{ph}_{xx}$. Let us estimate κ^{e}_{xx} by assuming that the Wiedemann-Franz law is valid at T_c. We obtain $\kappa^{e}_{xx}/T = L_0/\rho = 1.6 \times 10^{-2}$ W/K^{2}m ~ 8.4 % of κ_{xx}/T, indicating a predominant phononic contribution above T_c. Here, $L_0 = 2.44 \times 10^{-8}$ WΩ/K^2 is the Lorentz number and $\rho = 150$ $\mu\Omega$cm. Interestingly, a similar increase and its field suppression are observed in hole-doped $Ba_{1-x}K_xFe_2As_2$ [8] as well as in unconventional superconductors such as $YBa_2Cu_3O_{7-\delta}$[9] and $CeCoIn_5$,[10] originating from the enhancement of the QP mean-free path in the superconducting state. It should be noted that the enhancement factor $\kappa_{xx}(T_c/2)/\kappa_{xx}(T_c)$ in $Ba_{1-x}K_xFe_2As_2$[8] is two times larger than that in our result. The origin of this discrepancy will be discussed below.

To examine the electronic contribution to heat transport, we quantitatively estimated κ^{e}_{xx} and κ^{ph}_{xx} in the superconducting state from the field dependence of the thermal conductivity $\kappa_{xx}(B)$ (inset of Fig. 1). The data can be well described by the vortex-scattering model[8,11]

$$\kappa_{xx}(T,B) = \frac{\kappa^{e}_{xx}(T)}{1+\alpha(T)B} + \kappa^{ph}_{xx}(T), \tag{1}$$

where $\alpha(T)$ is an inverse field scale. In the analysis, $\kappa^{ph}_{xx}(T)$ and $\kappa^{e}_{xx}(T)$ are fixed to be field$-$independent by assuming that the condensate amplitude is nearly unaffected by mag-

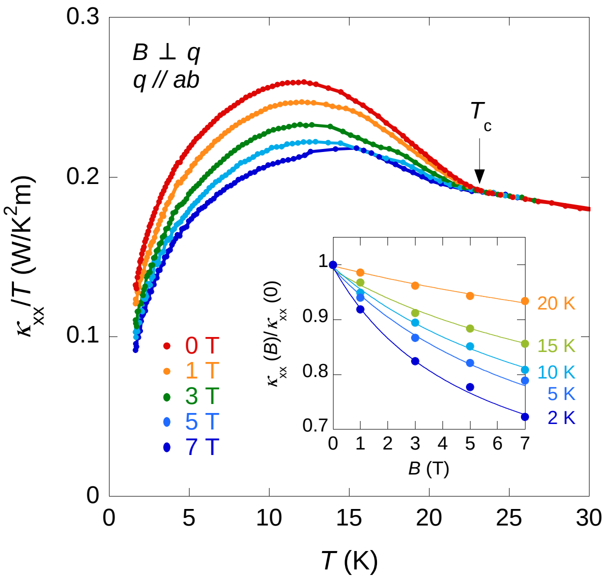

Fig. 1. (Color online) Temperature dependence of thermal conductivity $\kappa_{xx}(T)/T$ under several magnetic fields for $B \perp q$ and $q \| ab$. Inset: Field dependence of normalized thermal conductivity $\kappa_{xx}(B)/\kappa_{xx}(0)$ at fixed temperatures. Solid lines are fittings by the vortex scattering model (see text).

netic field at $B \leq 7$ T.[12] Figure 2(a) shows the temperature dependences of $\kappa^{\mathrm{e}}_{xx}(T)/T$ and $\kappa^{\mathrm{ph}}_{xx}(T)/T$ determined by fitting the data using eq. (1). It is noteworthy that $\kappa^{\mathrm{e}}_{xx}(T)/T$ exhibits a maximum at around $T_{\mathrm{c}}/2$ similar to $\kappa_{xx}(T)/T$. This implies that the peak in κ_{xx}/T at zero field is associated with κ^{e}_{xx}. The fittings also provide $\alpha(T)$, which is proportional to the QP mean-free path l through the relation $\alpha(T) = l\sigma_{\mathrm{tr}}/\Phi_0$,[11] where the cross section σ_{tr} is roughly equal to the coherence length ξ and Φ_0 is the flux quantum. In the inset of Fig. 2(b) (left axis), we show the temperature dependence of $\alpha(T)$, which exhibits a steep increase below T_{c}. This reflects an enhancement of l in the superconducting state. At 2 K, l is found to be $\sim$ 1100 Å with $\xi \simeq 34$ Å from $H^0_{c2} \sim 30$ T.[13]

Alternatively, the enhancement of the QP mean-free path can be confirmed from the thermal Hall conductivity κ_{xy}, which is a powerful probe for QPs since it is purely electronic. Figure 3(a) presents the field dependence of $|\kappa_{xy}|(B)$ at fixed temperatures. The sign of $\kappa_{xy}(B)$ is negative, consistent with that in electron doping opposite to the hole-doped $\mathrm{Ba_{1-x}K_xFe_2As_2}$.[8] In Fig. 2(b), we plot the temperature dependence of the initial slope $|\kappa^0_{xy}|/B \equiv \lim_{B\to 0} |\kappa_{xy}|/B$. As is clearly seen, $|\kappa^0_{xy}|(T)/B$ peaks at around $T_{\mathrm{c}}/2$ similar to the temperature dependence of $\kappa_{xx}(T)/T$. This directly indicates the enhancement of the electronic contribution to heat transport below T_{c}. In addition, the QP mean-free path is provided by the thermal Hall angle $\tan\Theta \equiv |\kappa_{xy}|/\kappa^{\mathrm{e}}_{xx}$ because $\tan\Theta/B \propto l$ in the weak field limit.[10] We plot the temperature dependence of $\tan\Theta/B$ in the inset of Fig. 2(b) (right axis). Clearly, $\tan\Theta/B$ increases with decreasing temperature, as we found in $\alpha(T) \propto l$. Therefore, all data consistently point to

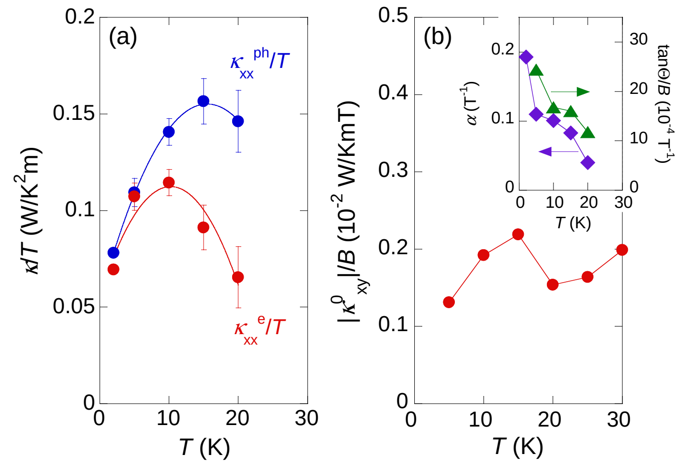

Fig. 2. (Color online) (a) Temperature dependence of electronic term $\kappa^{\rm e}_{xx}(T)/T$ and phononic term $\kappa^{\rm ph}_{xx}(T)/T$ of thermal conductivity. (b) Temperature dependence of initial slope of thermal Hall conductivity $|\kappa^0_{xy}|/B \equiv \lim_{B\to 0} |\kappa_{xy}|/B$. Inset: Temperature dependence of $\alpha(T)$ (left axis) and thermal Hall angle $\tan\Theta/B$ (right axis).

the striking enhancement of l below $T_{\rm c}$. This, in turn, suggests that l in the normal state is suppressed by the inelastic scattering possibly due to antiferromagnetic (AF) fluctuations, as discussed in the microwave conductivity measurements.[14] On the other hand, in the superconducting state, electrons condense into Cooper pairs and their number decreases rapidly below $T_{\rm c}$. This in turn gives rise to a reduction in the scattering cross section of QPs, and hence l increases below $T_{\rm c}$. The presence of AF fluctuations has also been indicated by recent NMR measurements.[7]

The thermal Hall conductivity κ_{xy} also provides the density of states of delocalized QPs, $N_{\rm del}(E)$, using the conjectures $\kappa^{\rm e}_{xx} \propto N_{\rm del}(E)l$ and $|\kappa_{xy}|/\kappa^{\rm e}_{xx}B \propto l$. A plot of ${\kappa^{\rm e}_{xx}}^2B/|\kappa_{xy}|$ as a function of field reveals the field dependence of $N_{\rm del}(E)$. Note that the precise estimation of $N_{\rm del}(E)$ from specific heat is rather difficult in iron pnictides because of the contribution of the nuclear Schottky anomaly.[15] As seen in Fig. 3(b), ${\kappa^{\rm e}_{xx}}^2B/|\kappa_{xy}|$ shows a weak field dependence within the experimental error of $|\kappa_{xy}|$, in contrast to the strong field dependence observed in nodal superconductors.[10] One may expect such a weak field dependence in fully gapped superconductors because QPs localized around vortex cores do not contribute to thermal conductivity at low fields $B \ll H_{\rm c2}$.

Next, we discuss the low-temperature thermal conductivity to gain insight into the superconducting pairing symmetry. We present the temperature dependence of the thermal conductivity $\kappa_{xx}(T)$ down to 0.1 K under zero magnetic field in Fig. 4. The lower inset of Fig. 4 shows the low-temperature part of the κ_{xx}/T vs T^2 plot. The straight line is a fit to $\kappa_{xx}/T = \kappa_0/T + bT^2$, where κ_0/T is the residual T-linear term extrapolated to $T \to 0$ K. The best fit was obtained with $\kappa_0/T = 1.2 \times 10^{-2}$ W/K^{2}m and $b = 0.33$ W/K^{4}m. What is surprising is that the residual T-linear term κ_0/T amounts to as much as half of the normal−state

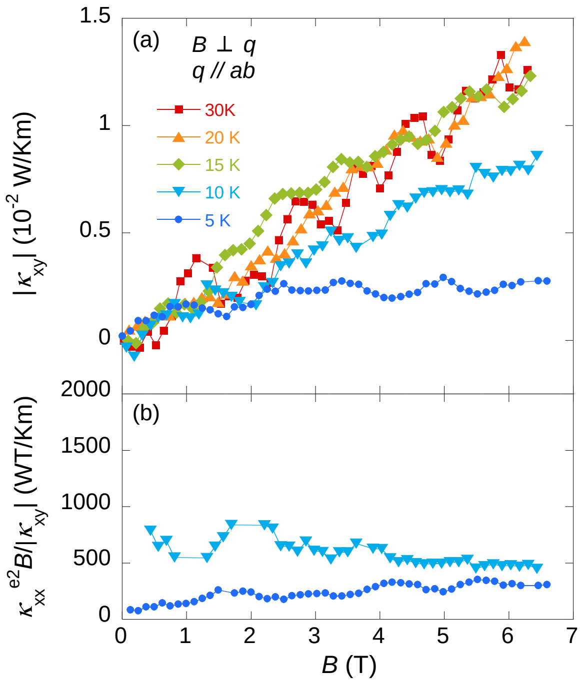

Fig. 3. (Color online) Field dependence of (a) thermal Hall conductivity $|\kappa_{xy}|(B)$ for $B \perp q$ and $q \| ab$ and (b) ${\kappa_{xx}^{\rm e}}^2 B/|\kappa_{xy}|$ which is proportional to the density of states of delocalized quasiparticles at fixed temperatures.

thermal conductivity $\kappa_{\rm n}/T$, which is estimated from the Wiedemann-Franz law as $\kappa_{\rm n}/T = L_0/\rho_0 = 1.9 \times 10^{-2}$ W/K^{2}m. Here, $\rho_0 = 130$ $\mu\Omega$cm is the residual resistivity at $T = 0$ K obtained by assuming that ρ decreases linearly against temperature below $T_{\rm c}$ (see dashed line in the upper inset of Fig. 4). On the other hand, using the mean acoustic phonon velocity $\langle v_s \rangle = 2400$ m/s and the phonon specific heat coefficient $\beta = 8.98$ J/K^{4}m^3 obtained from the parent compound of $BaFe_2As_2$,[16] the slope of $b = \frac{1}{3}\beta\langle v_s \rangle l_{\rm ph}$ yields $l_{\rm ph} = 46$ μm, which is the same order of magnitude as the smallest crystal dimension, namely, 40 μm thickness of the sample. This implies that the low-temperature thermal conductivity is dominated by phonons.

In the superconducting state, the presence of the residual T-linear term κ_0/T can be attributed to the impurity bound states formed by the interference of particle- and hole-like excitations, which undergo Andreev scattering, evoking sign changes of the order parameter as a result of unconventional pairing and impurity scattering. Moreover, in the nodal superconductors, κ_0/T takes a universal value independent of impurity concentration because the quasiparticles are both generated and scattered by the impurities.[17] In fact, the impurity concentration independent κ_0/T has been observed in high-$T_{\rm c}$ superconductors,[18] although its universality is still under debate.[19] Theoretically, the universal thermal conductivity κ_{00}/T

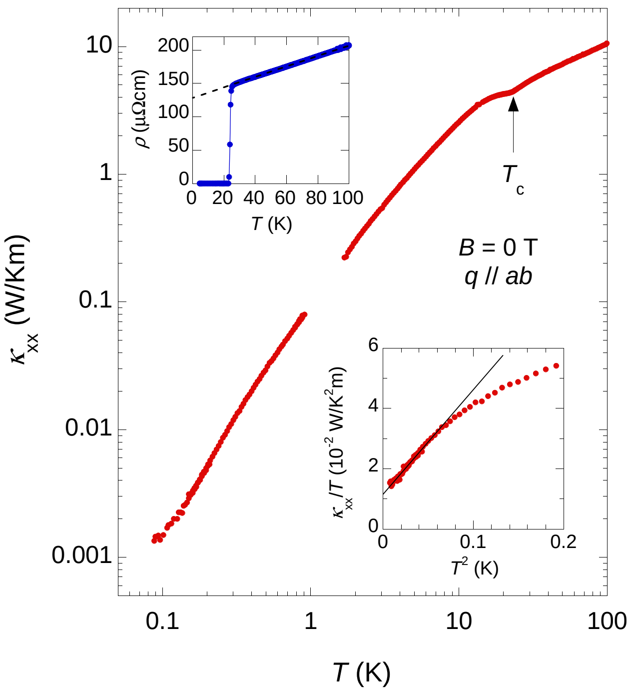

Fig. 4. (Color online) Temperature dependence of thermal conductivity $\kappa_{xx}(T)$ for $q \| ab$ under zero field. Upper inset: Temperature dependence of resistivity $\rho(T)$ under zero field. Lower inset: κ_{xx}/T vs T^2 plot under zero field. The solid line represents a fit to the data by $\kappa_{xx}/T = \kappa_0/T + bT^2$.

for the nodal superconductor is explicitly expressed as

$$\frac{\kappa_{00}}{T} = \frac{\pi^2}{3} N_f v_f^2 \times \frac{a\hbar}{2\mu\Delta_0}, \tag{2}$$

where N_f is the normal density of states, v_f is the Fermi velocity, Δ_0 is the maximum amplitude of the gap, μ is the slope of the gap at the node on the circular Fermi surface, and a is $\frac{4}{\pi}$ for the 2D order parameter with lines of nodes.[17] Using the Wiedemann-Franz law, eq. (2) can be written as $\frac{\kappa_{00}}{T} = \left(\frac{\pi}{4}\frac{2l\pi}{\xi}\frac{1}{\mu}\right)\frac{\kappa_n}{T}$.[20] By assuming a d-wave gap structure, we obtain $\kappa_{00}/T = 0.4 \times 10^{-3}$ W/K^{2}m for Ba(Fe$_{0.93}$Co$_{0.07}$)$_2$As$_2$ using $\mu = 2$ with $\xi = 34$ Å and $l =$ 1100 Å. The determined value is one order of magnitude smaller than the experimental value of κ_0/T. Although we cannot exclude the possibility of the nodal superconducting state on the basis of only κ_{00}/T, given the leading phononic contribution in low-temperature κ_{xx}, as evidenced by the T^3 term and the weak field dependence of N_{del}, nodal superconductivity is highly unlikely in Ba(Fe$_{0.93}$Co$_{0.07}$)$_2$As$_2$. Here, a question is raised as to how one can take a finite T-linear term in κ_{xx}/T without the nodal pairing state.

In addition to the nodal superconducting state, one can also expect a residual T-linear term in a novel s-wave pairing state. At first glance, the residual T-linear term seems to be incompatible with the s-wave state on the basis of Anderson's theorem.[21] On the contrary, it is possible to realize the finite value via impurity interband scattering between different Fermi surfaces with opposite signs of order parameters with full gaps. In fact, it is theoretically

proposed that the AF fluctuations with $\mathbf{Q} \approx (\pi, 0)$ resulting from the interband nesting between the hole and electron pockets realize a fully gapped sign-reversing s-wave state ($s_{\pm}$-wave state) in the iron pnictide superconductors.[4,5] In this state, the impurity-induced density of states (DOS) in the gaps is predicted to emerge when interband scattering is enhanced by the introduction of impurities.[22] However, it should be emphasized that such an in-gap state can be expected only if a strong impurity pair breaking involving a large reduction in T_c, which amounts to 10 K, occurs.[22]

Here, we discuss whether such a large reduction in T_c occurs in Co-doped $BaFe_2As_2$ to examine the possibility of the $s_{\pm}$-wave state in this system. Given that $T_c = 25$ K of Co-doped $BaFe_2As_2$ is about 10 K lower than that of the K-doped one, $T_c = 37$ K,[8] the difference in T_c can be explained by the difference in the strength of the pair breaking caused by the dopant. This is because the Co atoms substituted into the conducting layer can act as stronger pair breakers than the K atoms doped into the block layer. In fact, the enhancement of the thermal conductivity $\kappa_{xx}(T_c/2)/\kappa_{xx}(T_c)$ for $Ba(Fe_{0.93}Co_{0.07})_2As_2$ is reduced to half of that for K-doped $BaFe_2As_2$.[8] In addition, the resistivity at T_c for $Ba(Fe_{0.93}Co_{0.07})_2As_2$ ($\rho = 150\ \mu\Omega$cm) is three times larger than that for the K-doped one ($\rho = 50\ \mu\Omega$cm).[8] These results indicate that the scattering rate of $Ba(Fe_{0.93}Co_{0.07})_2As_2$ is practically enhanced by Co doping. In this case, one may expect the absence of an in-gap state or a smaller in-gap state in K-doped $BaFe_2As_2$ with weak scattering by the K atoms. Recently, a negligible residual T-linear term in κ_{xx}/T was found in $Ba_{1-x}K_xFe_2As_2$.[23] Moreover, the spin-lattice relaxation rate $1/T_1$ of the Co-doped $BaFe_2As_2$ appears to level off at low temperatures,[7] while that of the K-doped one varies close to T^3 all the way down to the lowest measured temperature.[24] These results further explain the role of Co atoms as strong pair breakers and support our scenario. Thus, our findings all point to the fully gapped $s_{\pm}$-wave state in $Ba(Fe_{0.93}Co_{0.07})_2As_2$, being consistent with the theoretical prediction as well as the resonance peak observed by the inelastic neutron scattering measurement.[25]

In summary, we uncovered an intriguing pairing state of the fully gapped sign-reversing s-wave state in the Co-doped $BaFe_2As_2$ by thermal transport measurements. Further experiments on samples with different Co doping levels are in progress to clarify the effect of inhomogeneity in the sample and the crucial role of non-magnetic impurities to the residual in-gap state.

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References

1) N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. W. Haselwimmer, and G. G. Lonzarich: Nature **394** (1998) 39.
2) Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono: J. Am. Chem. Soc. **130** (2008) 3296.
3) C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai: Nature **453** (2008) 899.
4) I. I. Mazin, SD. J. Singh, M. D. Johannes, and M. H. Du: Phys. Rev. Lett. **101** (2008) 057003.
5) K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki: Phys. Rev. Lett. **101** (2008) 087004.
6) Y. Nakajima, T. Taen, and T. Tamegai: J. Phys. Soc. Jpn. **78** (2009) 023702.
7) F. Ning, K. Ahilan, T. Imai, A. S. Sefat, R. Jin, M. A. Mcguire, B. C. Sales, and D. Mandrus: J. Phys. Soc. Jpn. **77** (2008) 103705.
8) J. G. Checkelsky, L. Li, G. F. Chen, J. L. Luo, N. L. Wang, and N. P. Ong: arXiv: 0811.4668.
9) Y. Zhang, N. P. Ong, P. W. Anderson, D. A. Bonn, R. Liang, and W. N. Hardy: Phys. Rev. Lett. **86** (2001) 890.
10) Y. Kasahara, Y. Nakajima, K. Izawa, Y. Matsuda, K. Behnia, H. Shishido, R. Settai, and Y. Onuki: Phys. Rev. B **72** (2005) 214515.
11) K. Krishana, N. P. Ong, Y. Zhang, Z. A. Xu, R. Gagnon, and L. Taillefer: Phys. Rev. Lett. **82** (1999) 5108.
12) Fittings using only the low-field data ($B \leq 3$ T) give values within the error bar shown in Fig. 2(a).
13) N. Ni, M. E. Tillman, J.-Q. Yan, A. Kracher, S. T. Hannahs, S. L. Bud'ko, and P. C. Canfield: Phys. Rev. B **78** (2008) 214515.
14) K. Hashimoto, T. Shibauchi, T. Kato, K. Ikada, R. Okazaki, H. Shishido, M. Ishikado, H. Kito, A. Iyo, H. Eisaki, S. Shamoto, and Y. Matsuda: Phys. Rev. Lett. **102** (2009) 017002.
15) A. Leithe-Jasper, W. Schnelle, C. Geibel, and H. Rosner: Phys. Rev. Lett. **101** (2008) 207004.
16) A. S. Sefat, M. A. McGuire, R. Jin, B. C. Sales, D. Mandrus, F. Ronning, E. D. Bauer, and Y. Mozharivskyj: Phys. Rev. B **79** (2009) 094508.
17) M. J. Graf, S.-K. Yip, J. A. Sauls, and D. Rainer: Phys. Rev. B **53** (1996) 15147.
18) L. Taillefer, B. Lussier, R. Gagnon, K. Behnia, and H. Aubin: Phys. Rev. Lett. **79** (1997) 483.
19) X. F. Sun, S. Ono, Y. Abe, S. Komiya, K. Segawa, and Y. Ando: Phys. Rev. Lett. **96** (2006) 017008.
20) K. Izawa, Y. Kasahara, Y. Matsuda, K. Behnia, T. Yasuda, R. Settai, and Y. Onuki: Phys. Rev. Lett. **94** (2005) 197002.
21) P. W. Anderson, J. Phys. Chem. Solids **11** (1959) 26.
22) Y. Senga and H. Kontani: New J. Phys. **11** (2009) 035005.
23) X. G. Luo, M. A. Tanatar, J.-Ph. Reid, H. Shakeripour, N. Doiron-Leyraud, N. Ni, S. L. Bud'ko, P. C. Canfield, H. Luo, Z. Wang, H.-H. Wen, R. Prozorov, and L. Taillefer: arXiv: 0904.4049.
24) H. Fukazawa, T. Yamazaki, K. Kondo, Y. Kohori, N. Takeshita, P. M. Shirage, K. Kihou, K. Miyazawa, H. Kito, H. Eisaki, and A. Iyo: J. Phys. Soc. Jpn. **78** (2009) 033704.
25) A. D. Christianson, E. A. Goremychkin, R. Osborn, S. Rosenkranz, M. D. Lumsden, C. D. Malliakas, I. S. Todorov, H. Claus, D. Y. Chung, M. G. Kanatzidis, R. I. Bewley, and T. Guidi: Nature **456** (2008) 930.